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ARTICLE TYPE

# Anion Receptor Coordination Tripods Capped by [9]aneS<sub>3</sub><sup>†</sup>

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A series of ruthenium(II) complexes with face-capping [9]ane-S<sub>3</sub> Ligands are described. The compounds function as supramolecular receptors for anions *via* three tripodally arranged 3-aminopyridine ligands. The [9]ane-S<sub>3</sub> ligand stabilises the tripodal complexes which are more readily prepared and studied than their  $\pi$ -arene ruthenium(II) analogues. Pyrenyl derivative **4** displays some activity as a photophysical anion sensor but the anion response is complicated by the complexes concentration dependent emission behaviour. The receptors bind common anions in relatively polar media forming both 1:1 and 1:2 host-anion complexes with the CH $\cdots$ anion interactions involving the thioether ring being implicated in anion binding as well as the convention NH donors.

## Introduction

The use of an octahedral metal centre as the core of a tripodal anion receptor compound has already received some attention owing to the well-defined geometries possible with the inclusion of metal ions the potentially rich redox and luminescence properties of coordination complexes.<sup>1-4</sup> Generation of a symmetric, metal-organic receptor can be achieved in one of two ways. One is to coordinate three ditopic ligands in a manner related to the well-documented ruthenium or iridium tris-2,2'-bipyridyl (bipy) complexes.<sup>5-7</sup> Substitution onto the bipy<sup>8-11</sup> or replacement of one bipy group with a similar species, for example biimidazole,<sup>12, 13</sup> can allow for pendant functional groups which can contain anion binding moieties in a suitable arrangement to engender anion selectivity. The second method relies on blocking three coordination sites of the octahedral metal centre in a facial (*fac*) manner such that the opposite three sites are positioned in a mutually orthogonal fashion to generate a tripodal anion binding pocket. The best method for achieving such blocking is through the use of a tridentate face-capping ligand, often an arene,<sup>14-16</sup> heterocycle,<sup>17, 18</sup> or claw-like tridentate ligand.<sup>19, 20</sup> Such a capped metal leads to the range of complexes known as 'half-sandwich' or 'piano-stool' complexes, named for their distinctive three-legged appearance.

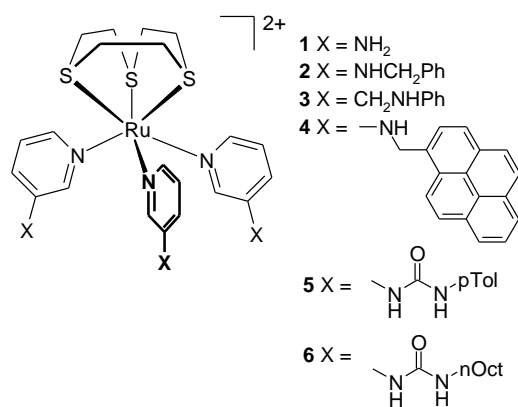
The metal ion itself must be relatively inert and exhibit a well-defined preference for an octahedral coordination geometry. In addition a diamagnetic centre is desirable from the point of view of NMR spectroscopic characterisation. These requirements tend to favour low-spin d<sup>6</sup> centres such as molybdenum(0), rhenium(I), ruthenium(II), rhodium(III) and iridium(III).<sup>14, 15, 21-25</sup>

Square planar palladium(II) and platinum(II) species have been used to form dipodal and tetrapodal molecular tweezers,<sup>14, 26-28</sup> and other more labile ion such as silver(I) have also been investigated.<sup>29-31</sup>

In previous work we have produced a range of ruthenium(II) dipodal receptors in which an  $\eta^6$ -arene ligand caps three *fac* coordination site of the octahedral metal centre. Anion binding occurs *via* two amino- or ureidopyridine ligands while the remaining coordination site is occupied by a chloride ligand.<sup>32, 33</sup> Synthesis of analogous tripodal complexes is hampered by steric interactions between the three pyridyl ligands, rendering the complexes relatively labile and hence anion complexation studies focussed on the dipodal analogues.<sup>34</sup> In the present work we report the synthesis of tripodal tris(pyridyl) ruthenium(II) dicationic receptors in which the hexahapto *p*-cymene capping group is replaced by the 1,4,7-trithiacyclononane ([9]ane-S<sub>3</sub>) heterocycle first reported by Schröder and coworkers<sup>35</sup> and later by Roche and *et al.*<sup>34, 36</sup> who achieved coordination of three pyridyl ligands to a [9]ane-S<sub>3</sub> capped ruthenium(II) centre. We anticipate therefore that use of the ([9]ane-S<sub>3</sub>)Ru(II)<sup>2+</sup> moiety should allow for the synthesis of tripodal receptors of well-defined geometry. Anion binding by CH $\cdots$ anion interactions within the coordinated [9]ane-S<sub>3</sub> crown has recently been reported by Bedford and co-workers and offers an interesting additional potential anion binding site.<sup>37</sup>

## Results and Discussion

### Synthesis and Structure



**Scheme 1**  $[(9)\text{ane-S}_3]\text{Ru}^{2+}$  receptor complexes synthesised in this study. Counter-ions are  $\text{PF}_6^-$  in each case.

Synthesis of the  $[9]\text{ane-S}_3$ -capped precursor  $[\text{Ru}([9]\text{ane-S}_3)\text{Cl}_2(\text{DMSO})]$  is readily achieved readily by reaction of  $[\text{RuCl}_2(\text{DMSO})_4]$ <sup>38</sup> with the thioether. The thioether displaces three of the coordinated DMSO molecules and remains coordinated to the ruthenium centre with a high degree of stability, although coordinated pyridines in the resulting  $[9]\text{ane-S}_3$  complexes can be displaced in the presence of acetonitrile.<sup>36</sup> Metathesis of the counter anions from chloride to hexafluorophosphate was achieved through addition of  $\text{AgPF}_6$  and subsequent removal of the precipitated  $\text{AgCl}$  to give an activated solvate complex which was used *in situ*. Addition of a range of 3-substituted pyridine ligands gave complexes **1** – **6** (Scheme 1), containing either a secondary amine or a urea as the anion binding functionality. In most cases, the complexes appear green in colour, with the exception of the pyrene-containing **4**, which is yellow-ochre. Some problems with purification arose during synthesis of the urea-based receptors **5** and **6** due to the similar solubilities of receptor complex and unbound ligand. These difficulties arose due to the need to have an excess of the ligand present in solution during the reaction to favour formation of the tripod – a threefold excess was found to be insufficient, producing a mixture of three-armed receptor, two-armed receptor, and free ligand. Addition of between 3.5 and 4 equivalents of ligand led to a greater yield of the desired three-armed receptor complexes **5** and **6**, but required removal of the excess ligand. For complex **5** this was achieved by dissolution of the crude product in acetone and addition of cold diethyl ether until the complex precipitated. Complex **6** required more careful solvent balance, eventually involving a mixture of acetone, diethyl ether and ethyl acetate to remove the majority of the excess ligand by

recrystallisation, although some ligand was still found to be present by  $^1\text{H-NMR}$  spectroscopy. As a result studies on **6** were not pursued.

Receptors **2** and **3** are isomers of one another, the difference being in the placement of the N-H group. Complex **3** potentially has a larger binding pocket within the receptor due to the extra distance from the core and the flexibility provided by the methylene bridge allowing a greater degree of encapsulation of an anion. Receptor **4**, with its pyrene functionalities, was designed as a potentially fluorescent anion sensor by analogy with related ‘pinwheel’ tripodal receptors.<sup>39</sup>

While analogous *p*-cymene-capped complexes were found to be stable as the dipodal species of type  $[\text{Ru}(p\text{-cymene})\text{L}_2\text{Cl}]^+$ ,<sup>32</sup> formation of the tripodal receptors  $[\text{Ru}(p\text{-cymene})\text{L}_3]^{2+}$  proved difficult, as a result of steric crowding about the metal centre. By contrast, compounds **1**–**6** based on  $[9]\text{ane-S}_3$  are significantly more stable than their  $\eta^6$ -arene counterparts with respect to solvolysis. Monitoring the  $^1\text{H-NMR}$  spectra of the complexes showed that after a period of one week in solution, only a small proportion (<10%) of the tripodal complex had degraded to form dipodal complex and free ligand. Even after four weeks, this ratio remains fairly constant, suggesting that the equilibrium tripod and dipod/free ligand is very slow on the NMR timescale and favours the tripodal species.

Complex **1** was obtained as single crystals from the ethanol:water reaction mixture and was characterised by single crystal X-ray crystallography, Figure 1. The structure adopts space group *P*1, with an inversion centre linking two complexes into an interdigitated dimer. These two symmetry-equivalent complexes are held together by the hydrogen bond interactions between the aminopyridine groups and two symmetry-related  $\text{PF}_6^-$  counter ions, resulting in a tripodal binding pocket for each anion. These anions also interact with the thioether ring of another symmetry equivalent receptor, in a similar manner to that described by Bedford and coworkers,<sup>37</sup> such that the anion is involved in six hydrogen bonds, three from N-H groups and three from C-H groups. The second symmetry-independent  $\text{PF}_6^-$  anion only engages in one N-H...F hydrogen bond (to N(6)H), but is surrounded by three thioether rings, which interacts with the anion *via* CH...F interactions. The NH...F distances 3.14 – 3.41 Å are relatively long compared to typical contacts found in the CSD for NH hydrogen bond donors hydrogen bonding to  $\text{PF}_6^-$  which are typically around 3.0 Å, and this may reflect the bifurcation of both the donors and acceptor. The CH-anion distances are in the range of 3.1 – 3.5 Å and are consistent with related systems in the CSD.

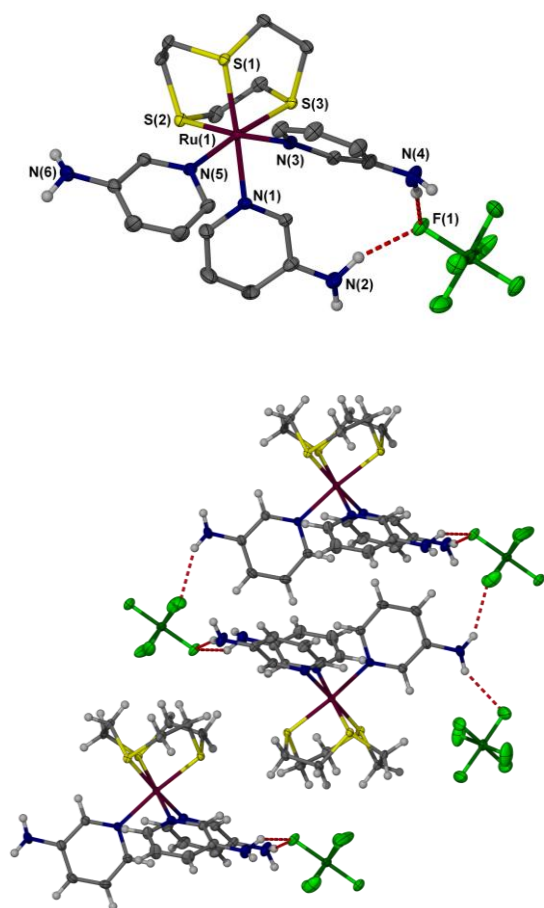


Figure 1 (a) X-ray molecular structure of **1** with hydrogen atoms attached to carbon removed for clarity. Selected H-bond distances ( $\text{\AA}$ ): N(4)H-F(1) 3.359(3); N(2)H-F(1) 3.138(3); N(6)H-F(7) 3.408(3). (b) Crystal packing in **1** (50% ellipsoids, CH hydrogen atom omitted for clarity).

The structure shows that the receptor complex, at least in the solid state, exists in the opposite conformation to that expected, with the aminopyridine N-H groups pointing away from a common cavity beneath the metal centre, though this may be an effect of the solid state packing in combination with the relatively large size of the  $\text{PF}_6^-$  anion. It seems plausible that rotation about the Ru-N axes could lead to a situation in which three amine N-H groups point to a central position.

## 10 Anion Binding Studies

Binding studies were performed on the receptor complexes using  $^1\text{H}$ -NMR spectroscopic titration in 30%  $\text{DMSO-d}_6$  /  $\text{CDCl}_3$  mixture. The inclusion of DMSO was essential to retain solubility of receptor **1** during the titration, as addition of anions to the solution in  $\text{CDCl}_3$  or acetone- $\text{d}_6$  caused precipitation of the complex. For consistency the same solvent system was used throughout the experiments.

Complex **1** showed marked broadening of the amine NH

resonances upon addition of anions caused either by rotation of the amine group about the C-N bond on a similar timescale to the NMR spectroscopic experiment or, more probably, by amine proton exchange. Similar difficulties were found during experiments with **3**, which also experiences increasingly significant broadening as the titration progresses. It is likely that hydrogen bonding to the anion increases the amine acidity. In these cases, the neighbouring pyridyl C-H signal (Hc, Figure 2) alone was followed during the titration, while for the other amine receptors (**2** and **4**) the N-H resonance remained sharp in the NMR spectrum and thus could be monitored. In titrations with **4**, only the NH resonance was monitored, as the pyridyl CH signal is obscured by the pyrene CH resonances. The NMR spectrum of **4** proved concentration dependent and a dilution study gave a dimerization constant of 2.63(8) which was included as a constant in anion complexation titrations. Titrations with urea-based receptor **5** followed the urea NH resonances exclusively. Job plot analyses suggested a mixture of 1:1 and 1:2 binding in many cases (Figure 4) and as a result a model including both 1:1 and 1:2 host:anion species proved to be a better fit to the data in most cases. Titration results are summarised in Table 1.

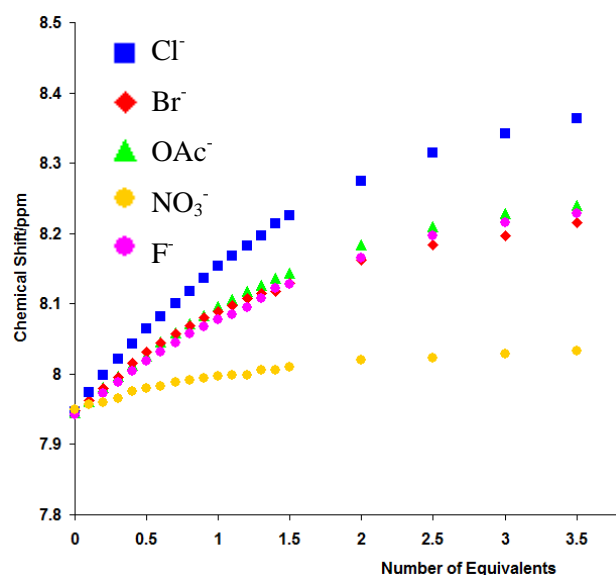


Figure 2. Chemical shift changes of pyridyl CH resonance of **1** with a variety of anions.

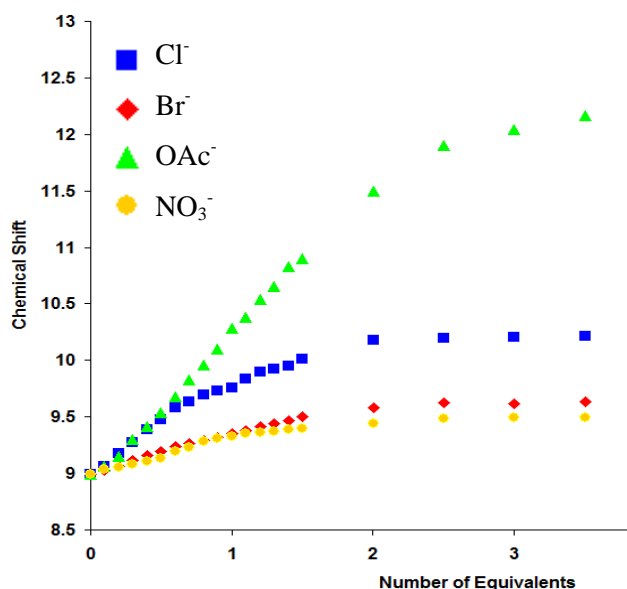


Figure 3 Chemical shift change of urea N-H resonance of **5** with a variety of anions.

Guest		Host				
		<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
OAc <sup>-</sup>	$\beta_1$	2.02(1)	2.05(1)	2.09(7)	2.36(1)	2.5(1)
	$\beta_{12}$	3.83(1)	3.90(2)	-	4.05(1)	5.84(3)
	( $K_2$ )	1.81	1.85	-	1.69	3.34
Br <sup>-</sup>	$\beta_1$	2.04(8)	2.29(8)	1.8(1)	2.68(3)	3.2(1)
	$\beta_{12}$	-	-	-	5.56(5)	6.29(9)
	( $K_2$ )	-	-	-	2.88	3.09
Cl <sup>-</sup>	$\beta_1$	1.76(1)	1.73(1)	2.2(1)	2.48(3)	3.2(1)
	$\beta_{12}$	3.52(1)	3.46(9)	-	4.6(1)	5.9(2)
	( $K_2$ )	1.76	1.73	-	2.12	2.7
F <sup>-</sup>	$\beta_1$	< 1	-	-	-	-
	$\beta_{12}$	-	-	-	-	-
NO <sub>3</sub> <sup>-</sup>	$\beta_1$	1.86(2)	2.33(6)	3.2(1)	2.65(3)	3.4(1)
	$\beta_{12}$	-	-	-	-	5.3(3)

Table 1 Binding constants (given as log values) ([9]ane-S<sub>3</sub>)Ru-based hosts, showing 1:1 and 1:2 binding modes, refined using HypNMR 2006<sup>40</sup> in 30% DMSO-d<sub>6</sub> / CDCl<sub>3</sub> mixture. Titrations of receptor **1** with fluoride showed poor binding, so this anion was omitted from further studies.  $K_2$  is calculated by subtracting  $\beta_1$  from  $\beta_{12}$  (where applicable) and represents the second binding step. Data for **4** include the dimerization equilibrium, log  $K_{20}$  = 2.63(8).

From the titration data, it is possible to compare the anion affinities of the receptor complexes. There is only a small difference between the binding affinities of **1** and **2**, suggesting that the addition of a benzyl group to the receptor amine has only a marginal effect on the anion binding of the receptor. Interestingly, binding of both of these hosts shows little variation in strength for the addition of the first and second equivalent of anion, especially for chloride, suggesting that there is little cooperativity between ligands.

Changing the position of the N-H group has a much more

pronounced effect on the receptor properties. Anions typically bind in a 1:1 ratio with **3** compared to the mixture of 1:1 and 1:2 complexes formed by **2**. Compound **3** seems to show a slightly higher affinity for nitrate over the other anions (albeit with large error) perhaps reflecting the larger cavity. The inclusion of the sterically more demanding pyrenyl functionality seems to favour binding of the receptor to chloride (and to a lesser extent acetate), with chloride binding to receptor **4** approximately five to ten fold stronger compared to the smaller receptors **1** – **3**. Receptor **5** with its strongly anion binding urea groups is generally the most effective host. Unusually, receptor **5** appears to show strongest binding with bromide over the other anions studied, despite this anion showing only a small chemical shift change throughout the titration. The higher affinity for bromide compared to acetate may be due to the size and shape complementarity of the receptor to the anion – the spherical bromide is able to interact better with the three binding groups, but has only a small effect on the electronic shielding of the binding protons. The acetate titration data exhibit a marked sigmoidality (Figure 3) suggesting some degree of positive cooperativity in binding the second anion and indeed  $K_2$  is markedly higher than  $\beta_1$ . The origins of this effect are not clear but must reflect the more demanding shape of the acetate anion compared to spherical anions such as halides. The nitrate data also showed marked sigmoidality, albeit with a dramatically smaller chemical shift change. This data proved impossible to fit to a 1:1 and 1:2 binding model and a contribution from a 2:1 host:guest species was also included,  $\beta_{21}$  = 6.5(3) to model the data however the fit remained unsatisfactory.

Overall, the complexes show significantly higher affinity than related metal complexes with only a single pyridyl ligand,<sup>23</sup> which are found to bind only very weakly. This is likely to be a reflection of the multiple binding groups and positive charge.

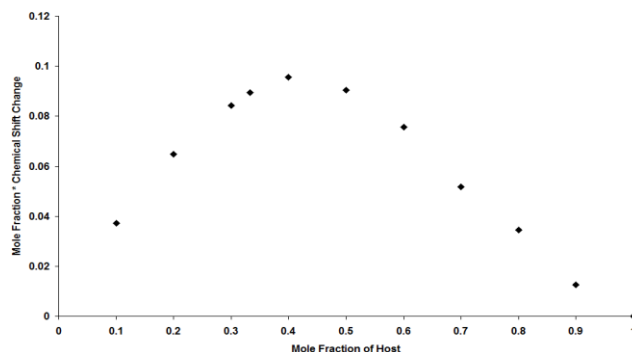


Figure 4 Job plot for receptor **1** with TBA chloride.

The presence of a 1:2 host:guest species in many cases may indicate the possibility of anions either binding separately to different pyridyl ligands or nestling within the CH binding pocket of the [9]ane-S<sub>3</sub> in a similar way to the X-ray crystal structure of **1** and the related [9]ane-S<sub>3</sub> capped palladium complex.<sup>37</sup> The presence of two different binding modes is consistent with the broadening of the NH resonances observed during some of the NMR titration experiments. Further evidence for the involvement of the [9]ane-S<sub>3</sub> CH protons comes from the observation that the resonances assigned to these protons undergo noticeable chemical shift change of up to 0.5 ppm during the titration.

## Photophysical Studies

Receptor **4** is expected to be fluorescent due to the presence of the photoactive pyrenyl groups.<sup>39, 41–44</sup> The complex shows an absorbance spectrum similar in structure to that of the free pyrenyl pyridine ligand from which it is derived, albeit red-shifted slightly (Figure 5), suggesting a lowering in the excitation energy caused by coordination to the metal. As expected, the molar extinction coefficient of **4** is approximately three times greater than that of the free ligand, due to the complex containing three coordinated ligands.

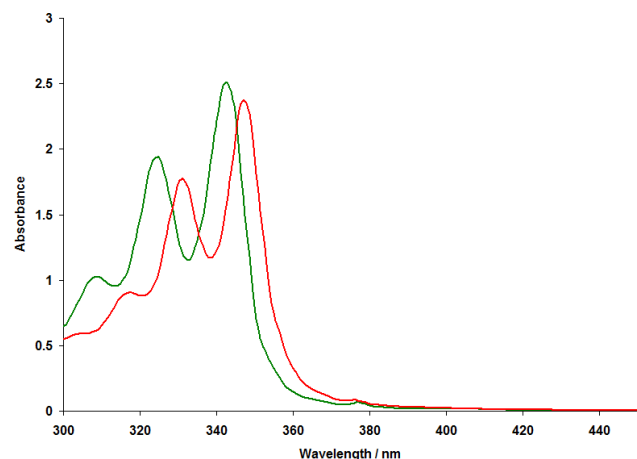


Figure 5 UV/Visible absorption profiles of **4** ( $2 \times 10^{-5} \text{ mol dm}^{-3}$ , red) and unbound 3-(1-pyrenemethylamino)pyridine ( $6 \times 10^{-5} \text{ mol dm}^{-3}$ , green) in 30% DMSO /  $\text{CHCl}_3$  solvent.

Addition of anions to the solution had a negligible impact on the absorption spectrum of the complex. This lack of detectable spectral response to the addition of most anions indicates that the hydrogen bonding functionalities are not electronically coupled to the pyrene chromophore.

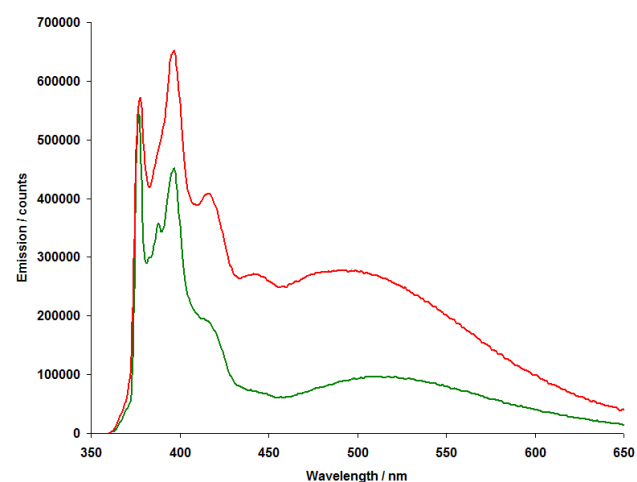


Figure 6 Emission profiles for **4** ( $4 \times 10^{-6} \text{ mol dm}^{-3}$ , red) and unbound 3-(1-pyrenemethylamino)pyridine ( $1.2 \times 10^{-5} \text{ mol dm}^{-3}$ , green) in 30% DMSO /  $\text{CHCl}_3$  solvent, excitation wavelength of 347 nm.

Excitation of **4** at the primary absorbance wavelength at 347 nm

results in primarily emission assignable to a monomeric pyrene derivative which shares similarities to the free ligand (Figure 5). Both free ligand and complex **4** exhibit broad bands to longer wavelength assignable to pyrene excimer emission.<sup>45</sup> This band occurs at 511 nm for the free ligand, while the excimer band for **4** appears to involve two overlapping excimeric species, possibly intra- and intermolecular excimers. The intensity of the excimer band is significantly higher in the case of **4** than the free ligand (at the same concentration). The most feasible explanation is that the band is enhanced by the pyrene groups being forced into close proximity to one another through their coordination to the metal, thus encouraging excimer formation. Addition of acetate, nitrate, chloride and bromide anions to the solution of **4**, when followed by fluorimetry, at first glance appears to have a switch-on effect on the emission of the complex, with the emission intensity at 397 nm increasing to almost double the initial value, accompanied by a similar increase in the 500 nm excimer band. Further investigation into this enhancement, however, showed that this is not purely anion driven – a similar emission profile to those found with anions is found from the complex alone at the reduced concentration experienced at the end of the titration experiment (Figure 6). The increase in emission at lower concentration suggests that some degree of quenching is taking place for receptor **4**, since the same effect is not observed for the free ligand.

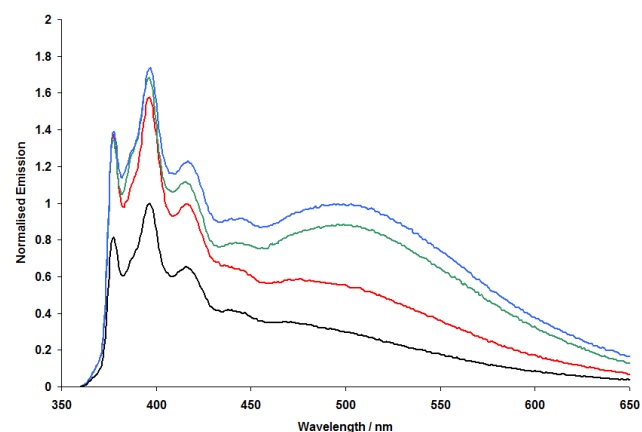


Figure 7 Normalised emission profiles for **4** (red) and with chloride (green) and acetate (blue) at  $4.3 \times 10^{-5} \text{ mol dm}^{-3}$  in 30% DMSO /  $\text{CHCl}_3$ . All three spectra have been normalised relative to the standard before dilution (**4** at  $5 \times 10^{-5} \text{ mol dm}^{-3}$ , black) because of the concentration dependence of the complex's emission intensity.

In order to determine the degree of this quenching, the emission intensity of the complex was recorded at a range of concentrations, and in a varying ratio of DMSO: $\text{CHCl}_3$  solvent. Dilution of the complex, keeping the solvent ratio the same, follows a non-linear progression, with the highest intensity of emission being observed at extremely low complex concentration (Figure 7). Below this critical concentration the emission intensity falls off rapidly. Collecting absorbance data over the same range of concentrations shows a linear change in the absorbance with concentration suggestion that the quenching effect is not a result of dimerization or aggregation.



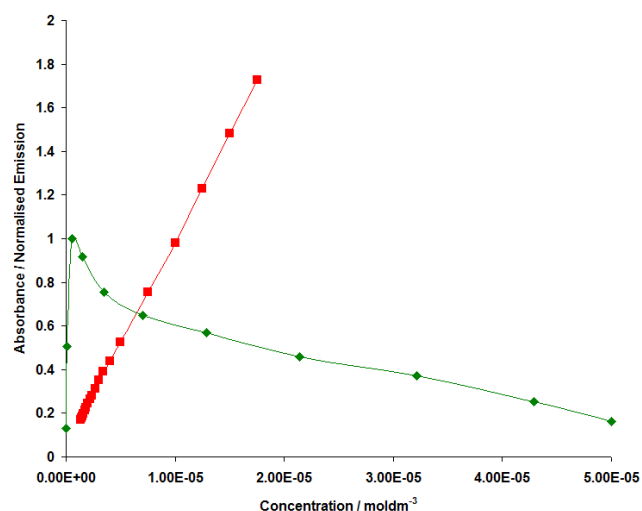


Figure 8 Absorbance (red) at 347 nm and emission (normalised, green) and 397 nm of **4** as a function of concentration in 30% DMSO / CHCl<sub>3</sub>.

It was also found that the emission quenching was more significant at lower DMSO content, and less evident in solvent mixtures with a higher proportion of DMSO, suggesting that ion pairing is a possible factor in the quenching process – ion pairing is expected to be less significant in the more polar solvent.

While the emission spectrum of the complex is thus highly dependent on the concentration of the complex, the relative intensity of the excimer emission band is affected by anions, Figure 8, with acetate giving the most marked effect on the ratio between monomer and excimer bands. An increase in the intensity of this band is observed depending on the identity of the added anion, indicating that the pyrene-pyrene interactions are somewhat influenced enhanced by anion binding. The same effect is not observed by titration of anions into a solution of free 20 3-(1-pyrenemethylamino)pyridine, and hence it must arise from the close proximity of the pyrenyl groups in the complex.

## Conclusions

In summary, a range of 1,4,7-trithiacyclononane-capped ruthenium(II)-based anion receptor complexes have been synthesised. These receptors, in contrast to similar  $\pi$ -arene capped ruthenium complexes, show a high resistance to degradation from the tripodal ML<sub>3</sub> species to a dipodal ML<sub>2</sub>X species by solvent or anion. The receptors bind common anions in relatively polar media forming both 1:1 and 1:2 host-anion complexes with the CH $\cdots$ anion interactions involving the thioether ring being implicated in anion binding as well as the conventional NH donors. Attempts to produce a fluorescent anion sensor based on appended pyrenyl groups were only partially successful because of complications arising from the concentration dependence of the host emission.

## Experimental

### Synthesis

Pyridine-containing ligands were synthesised according to previously published methods.<sup>14, 31, 32, 39</sup>

### [Ru([9]ane-S<sub>3</sub>)Cl<sub>2</sub>(DMSO)]

RuCl<sub>3</sub>·3H<sub>2</sub>O (1.00 g, 3.80 mmol) was dissolved in the minimum amount of DMSO (3 ml) and the solution heated to boiling to remove any water. The DMSO solution was cooled and acetone (25 ml) was added, leading to precipitation of a dark orange material. Filtration of this material left an orange solution which gave the desired RuCl<sub>2</sub>(DMSO)<sub>4</sub> as yellow crystals upon drying. Repeated dissolution of the dark orange precipitate with more DMSO/acetone with heating produced more of the yellow product. Yield 0.80 g, 1.6 mmol, 43%. Anal. Calc. for C<sub>8</sub>H<sub>24</sub>S<sub>4</sub>O<sub>4</sub>RuCl<sub>2</sub>: C, 19.83; H, 4.99. Found: C, 19.84; H, 4.90. The resulting RuCl<sub>2</sub>(DMSO)<sub>4</sub> (0.48 g, 1.0 mmol) was dissolved in CHCl<sub>3</sub> (25 ml) in a round-bottomed flask fitted with a reflux condenser. 1,4,7-Trithiacyclononane (0.20 g, 1.1 mmol) was added and the solution heated to reflux for 90 min with stirring, leading to the precipitation of [Ru([9]ane-S<sub>3</sub>)Cl<sub>2</sub>(DMSO)] as a yellow-orange solid. Yield 0.36 g, 0.84 mmol, 84%. Anal. Calc. for C<sub>8</sub>H<sub>18</sub>S<sub>4</sub>ORuCl<sub>2</sub>: C, 22.32; H, 4.21. Found: C, 22.05; H, 4.08.

### [Ru([9]ane-S<sub>3</sub>)(3-aminopyridine)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (**1**).

[Ru([9]ane-S<sub>3</sub>)Cl<sub>2</sub>(DMSO)] (0.17 g, 0.40 mmol) was dissolved in ethanol/water (1:1, 30 ml) with slight warming of the solution. Silver hexafluorophosphate (0.21 g, 0.85 mmol) was added and the solution stirred at 60°C for 1 h, over which time the formation of silver chloride could be observed as a grey precipitate. Filtration of this salt left a yellow solution, to which was added 3-aminopyridine (0.11 g, 1.2 mmol). The solution was then heated to reflux for 16 h, during which the colour turned from yellow to blue-green. Cooling and slow evaporation of the solvent led to the formation of the product as deep green needle-shaped crystals. Yield 0.13 g, 0.15 mmol, 37%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, J/Hz,  $\delta$ /ppm): 2.53 – 2.90 (m, 12 H, CH<sub>2</sub>), 5.79 (s, 6 H, NH<sub>2</sub>), 6.98 – 7.14 (m, 6 H, pyH), 7.41 (d, J = 4.5, 3 H, pyH), 7.73 (d, J = 2.2, 3 H, pyH). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>,  $\delta$ /ppm): 33.68, 122.46, 126.40, 139.96, 142.31, 146.96. ESI<sup>+</sup>-MS: m/z 708.8 [(9]ane-S<sub>3</sub>)Ru(3-aminopyridine)<sub>3</sub>PF<sub>6</sub>]<sup>+</sup>, 281.7 [(9]ane-S<sub>3</sub>)Ru(3-aminopyridine)<sub>3</sub>]<sup>2+</sup>. Anal. Calc. for C<sub>21</sub>H<sub>30</sub>N<sub>6</sub>S<sub>3</sub>Ru(PF<sub>6</sub>)<sub>2</sub>: C, 29.54; H, 3.54; N, 9.85. Found: C, 29.68; H, 3.60; N, 9.52. IR (cm<sup>-1</sup>): 3391 (v(N-H)).

### [Ru([9]ane-S<sub>3</sub>)(3-(benzylamino)pyridine)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (**2**).

[Ru([9]ane-S<sub>3</sub>)Cl<sub>2</sub>(DMSO)] (0.16 g, 0.38 mmol) was treated with silver hexafluorophosphate as described for **1**. The resulting yellow solution was treated with 3-(benzylamino)pyridine<sup>46</sup> (0.21 g, 1.1 mmol). The solution was then heated to reflux for 16 h, during which the colour turned from yellow to green. Cooling the solution and removal of the solvent *in vacuo* led to the formation of the product as a green powder. Yield 0.31 g, 0.27 mmol, 72%. <sup>1</sup>H NMR (acetone-d<sub>6</sub>, J/Hz,  $\delta$ /ppm): 2.59-3.02 (2 m, 12 H, thioether CH<sub>2</sub>), 4.24 (d, J = 5.6, 6 H, ligand CH<sub>2</sub>), 6.41 (t, J = 5.6, 3 H, NH), 7.13 – 7.38 (m, 15 H, pyH and ArH), 7.56 (d, J = 2.5, 3 H, pyH), 7.78 (d, J = 5.5, 3 H, pyH). <sup>13</sup>C{<sup>1</sup>H} NMR (Acetone-d<sub>6</sub>,  $\delta$ /ppm): 33.57, 46.70, 121.73, 126.36, 126.99, 127.42, 128.85, 138.37, 138.67, 141.77, 146.57. ESI<sup>+</sup>-MS: m/z 979.1 [M-PF<sub>6</sub>]<sup>+</sup>. Anal. Calc. for C<sub>42</sub>H<sub>48</sub>N<sub>6</sub>S<sub>3</sub>Ru(PF<sub>6</sub>)<sub>2</sub>: C, 44.87; H, 4.30; N, 7.48. Found: C, 45.15; H, 4.44; N, 7.36. IR (cm<sup>-1</sup>): 3442 (v(N-H)).

**[Ru([9]ane-S<sub>3</sub>)(3-(phenylaminomethyl)pyridine)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (3).**

[Ru([9]ane-S<sub>3</sub>)Cl<sub>2</sub>(DMSO)] (0.16 g, 0.38 mmol) was treated with silver hexafluorophosphate as described for **1**. The resulting yellow solution was treated with 3-(phenylaminomethyl)pyridine<sup>32</sup> (0.21 g, 1.1 mmol) to the solution of this intermediate, followed by heating to reflux for 16 h, led to a green colour. Cooling and removal of the solvent led to the formation of the product as a green powder. Yield 0.24 g, 0.22 mmol, 59 %. <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, J/Hz, δ/ppm): 2.55-2.70 (m, 6H, thioether CH<sub>2</sub>), 2.80-2.95 (m, 6H, thioether CH<sub>2</sub>), 4.39 (d, J = 6.2, 6H, ligand CH<sub>2</sub>), 5.60 (t, J = 6.2, 3H, NH), 6.40-6.55 (m, 6H, H<sub>b</sub>), 6.64 (t, J = 5.7, 3H, ArH), 7.09 (dd, J = 7.5, 8.3, 6H, ArH), 7.39 (dd, J = 5.7, 7.8, 3H, pyH), 8.03 (d, J = 7.7, 3H, pyH), 8.31 (d, J = 5.5, 3H, pyH), 8.39 (s, 3H, pyH). <sup>13</sup>C{<sup>1</sup>H} NMR (Acetone-d<sub>6</sub>, δ/ppm): 33.57, 44.15, 112.61, 117.26, 126.64, 129.38, 138.15, 139.72, 147.74, 152.41. ESI<sup>+</sup>-MS: m/z 979.2 [M-PF<sub>6</sub>]<sup>+</sup>. Anal. Calc. for C<sub>42</sub>H<sub>48</sub>N<sub>6</sub>S<sub>3</sub>Ru(PF<sub>6</sub>)<sub>2</sub>: C, 44.87; H, 4.30; N, 7.48. Found: C, 45.07; H, 4.42; N, 7.39. IR (cm<sup>-1</sup>): 3444 (ν(N-H)).

**[Ru([9]ane-S<sub>3</sub>)(3-(1-pyrenemethylamino)pyridine)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (4).**

[Ru([9]ane-S<sub>3</sub>)Cl<sub>2</sub>(DMSO)] (0.22 g, 0.50 mmol) was treated with silver hexafluorophosphate as described for **1**. The resulting yellow solution was treated with 3-(1-pyrenemethylamino)pyridine<sup>39</sup> (0.46 g, 1.5 mmol) was added to the solution and again heated to reflux for 16 h, causing the colour of the solution to go yellow-ochre in colour. Cooling and removal of the solvent led to the formation of the product as an ochre powder. Yield 0.59 g, 0.39 mmol, 79%. <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, J/Hz, δ/ppm): 1.96 – 2.50 (m, 12 H, thioether CH<sub>2</sub>), 4.64 (d, J = 5.5, 6 H, pyH), 6.43 (t, J = 5.5, 3 H, NH), 6.68 (dd, J = 5.5, 8.6, 3H), 7.02 (d, J = 5.5, 3H), 7.14 (d, J = 8.4, 3H), 7.27 (d, J = 5.5, 3H), 7.81 (d, J = 7.9, 3H), 8.00 – 8.28 (m, 18 H), 8.34 (dd, J = 1.9, 7.7, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (Acetone-d<sub>6</sub>, δ/ppm): 33.06, 44.55, 122.38, 124.58, 124.66, 124.94, 125.19, 125.55, 125.66, 125.72, 126.51, 127.40, 127.62, 127.94, 128.13, 130.78, 130.85, 131.11, 131.47, 137.49, 141.36, 146.07. ESI<sup>+</sup>-MS: m/z 1351.5 [M-PF<sub>6</sub>]<sup>+</sup>. Anal. Calc. for C<sub>72</sub>H<sub>60</sub>N<sub>6</sub>S<sub>3</sub>Ru(PF<sub>6</sub>)<sub>2</sub>: C, 57.78; H, 4.04; N, 5.62. Found: C, 57.10; H, 4.03; N, 5.52. IR (cm<sup>-1</sup>): 3428 (ν(N-H)).

**[Ru([9]ane-S<sub>3</sub>)(3-(*p*-tolylureido)pyridine)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (5).**

[Ru([9]ane-S<sub>3</sub>)Cl<sub>2</sub>(DMSO)] (0.16 g, 0.38 mmol) was treated with silver hexafluorophosphate as described for **1**. The resulting yellow solution was treated with 3-(*p*-tolylureido)pyridine<sup>31</sup> (0.27 g, 1.2 mmol) was added to the solution and again heated to reflux for 16 h, causing the colour of the solution to go dark green in colour. Cooling and removal of the solvent led to the formation of the crude product as a dark green powder. Purification was achieved by recrystallisation of this green powder with acetone/diethyl ether to remove excess ligand. The final product was a lighter shade of green than the crude. Yield 0.23 g, 0.19 mmol, 46%. <sup>1</sup>H NMR (acetone-d<sub>6</sub>, J/Hz, δ/ppm): 1.11 (s, 9 H, H<sub>k</sub>), 2.25-2.89 (m, 12 H, thioether CH<sub>2</sub>), 7.10 (d, J = 8.6, 6 H, ArH), 7.37 (d, J = 8.6, 6 H, ArH), 7.45 (dd, J = 5.7, 8.3, 3 H, pyH), 7.99 (d, J = 5.7, 3 H, pyH), 8.05 (d, J = 8.1, 3 H, pyH), 8.24 (s, 3H, pyH), 8.72 (s, 3 H, NH), 9.35 (s, 3 H, NH). <sup>13</sup>C{<sup>1</sup>H}

NMR (Acetone-d<sub>6</sub>, δ/ppm): 19.96, 33.85, 119.36, 126.82, 127.54, 129.51, 132.47, 136.43, 139.14, 144.38, 147.60, 152.46. MALDI-ToF<sup>+</sup>-MS: m/z 755.1 [(9]ane-S<sub>3</sub>)Ru(TUP)<sub>2</sub>F]<sup>+</sup>. Anal. Calc. for C<sub>45</sub>H<sub>51</sub>N<sub>9</sub>O<sub>3</sub>S<sub>3</sub>Ru(PF<sub>6</sub>)<sub>2</sub>: C, 43.13; H, 4.10; N, 10.06. Found: C, 42.94; H, 4.35; N, 9.49. IR (cm<sup>-1</sup>): 2923 (ν(N-H)), 1717 (ν(C=O)).

**[Ru([9]ane-S<sub>3</sub>)(3-(*n*-octylureido)pyridine)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (6).**

[Ru([9]ane-S<sub>3</sub>)Cl<sub>2</sub>(DMSO)] (0.16 g, 0.38 mmol) was treated with silver hexafluorophosphate as described for **1**. The resulting yellow solution was treated with 3-(*n*-octylureido)pyridine<sup>47</sup> (0.22 g, 0.9 mmol) was added to the solution, containing 0.3 mmol of ([9]ane-S<sub>3</sub>)Ru(PF<sub>6</sub>)<sub>2</sub>.DMSO and again heated to reflux for 16 h, causing the colour of the solution to go dark green in colour. Cooling and removal of the solvent led to the formation of the crude product as a dark green powder. Purification was difficult due to the high solubility of both OUP and the complex. Repeated recrystallisation of the crude product with acetone/cold diethyl ether was required to remove the majority of the starting material. Yield 0.22 g, 0.17 mmol, 55%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, J/Hz, δ/ppm): 0.83 – 3.03 (m, 51 H, octyl C-Hs), 6.41 (s, 3 H, H<sub>b</sub>), 7.31 (dd, J = 5.6, 8.4, 3 H, H<sub>c</sub>), 7.73 (d, J = 5.6, 3 H, H<sub>f</sub>), 7.91 (d, J = 8.4, 3 H, H<sub>d</sub>), 8.75 (s, 3 H, H<sub>c</sub>), 9.06 (s, 3 H, H<sub>g</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, δ/ppm): 14.33 – 40.71 (8 C, octyl Cs), 34.66 (thioether Cs), 127.41, 127.65, 140.49, 144.63, 147.64, 155.74 (urea C). ESI<sup>+</sup>-MS: m/z 799.1 [(9]ane-S<sub>3</sub>)Ru(OUP)<sub>2</sub>F]<sup>+</sup>. Anal. Calc. for C<sub>48</sub>H<sub>81</sub>N<sub>9</sub>O<sub>3</sub>S<sub>3</sub>Ru(PF<sub>6</sub>)<sub>2</sub>: C, 43.69; H, 6.19; N, 9.56. Found: C, 42.78; H, 5.97; N, 9.26. IR (cm<sup>-1</sup>): 2928 (ν(N-H)), 1680 (ν(C=O)).

**General Procedure for <sup>1</sup>H NMR spectroscopic titration**

A solution of the host species of known concentration typically 0.5-1.5 mM, was made up in an NMR tube using the appropriate deuterated solvent (0.5 ml CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub> (v/v 70/30)). Solutions of the anions, as TBA salts (1 ml) were made ten times the concentration of the host solution. The guest solution was typically added in 10 µl aliquots, representing 0.1 equivalents of the guest with respect to the host. Larger aliquots were used in some cases where no inflection of the trace was evident. Spectra were recorded after each addition and the trace was followed simultaneously. Results were analysed using the curve-fitting program HypNMR 2006.<sup>40</sup> For Job plot experiments stock solutions of host and guest concentration 1 mM were mixed in varying proportions to give a constant total volume and the NMR spectra recorded.<sup>48</sup>

**Photophysical Measurements**

UV-vis spectroscopic measurements were carried out using a Perkin-Elmer Lambda 35 spectrometer. Emission and excitation spectra were obtained using a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter with a right angle illumination method and were corrected for the spectral response of the instrument. Fluorescence spectroscopic titrations used a stock solution of concentration 1.0 x 10<sup>-4</sup> mol dm<sup>-3</sup> of host in a volumetric flask. A 3 ml sample of host solution was prepared by the desired dilution of the stock solution and titrated with the appropriate guest. Guest solutions were prepared such that 100 µl of guest solution corresponds to 100 equivalents of host.



## Crystal Data

Crystals were grown from 5.1 in Ethanol/water (1:1 ratio, 2 ml) by slow evaporation of the solvent. Crystal data for **1**:  $C_{21}H_{30}F_{12}N_6P_2RuS_3$ ,  $M = 853.70$ , green needles,  $0.02 \times 0.02 \times 0.2$  mm<sup>3</sup>, triclinic, space group  $P\bar{1}$  (No. 2),  $a = 11.7238(11)$ ,  $b = 11.7563(11)$ ,  $c = 13.1508(12)$  Å,  $\alpha = 109.9560(10)$ ,  $\beta = 94.499(2)$ ,  $\gamma = 110.922(2)^\circ$ ,  $V = 1549.4(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.830$  g/cm<sup>3</sup>,  $F_{000} = 856$ , MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $T = 120(2)$  K,  $2\theta_{max} = 61.0^\circ$ , 27777 reflections collected, 8829 unique ( $R_{int} = 0.0280$ ). Final  $Goof = 0.920$ ,  $RI = 0.0306$ ,  $wR2 = 0.1072$ ,  $R$  indices based on 7873 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), 430 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.910$  mm<sup>-1</sup>.

## Notes and references

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- <sup>†</sup> Dedicated to Prof. Peter C. Junk on occasion of his 50<sup>th</sup> Birthday.
- <sup>‡</sup> Electronic Supplementary Information (ESI) available: Additional titration isotherms and UV-Vis absorption spectra. See DOI: 10.1039/b000000x/
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